



Preparation of Entangled Polymer Melts of Various Architecture for Coarse-grained Models

by Yelena R. Sliozberg and Jan W. Andzelm

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Preparation of Entangled Polymer Melts of Various Architecture for Coarse-grained Models

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14. ABSTRACT <p>Most of the practically useful polymers have molecular weight range from 20,000 to 200,000. Mechanical properties of these polymers are dominated by topological constraints or entanglements. Direct brute-force equilibration of well-entangled polymers is still unattainable because of slow reptation dynamics. In this technical report, we have introduced a new fast protocol to prepare well-equilibrated entangled polymeric systems of various compositions and architectures. Our algorithm is simple to implement and it is general for any coarse-grained polymer model. The present preparation method exploits two programs: <i>gel</i> and Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). This report presents a theory overview and a manual how to use the method.</p>					
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1. Overview

Equilibration of entangled polymers is nontrivial even for a case of coarse grained chains because of slow reptation dynamics exhibited by high molecular weight chains, where center-of-mass diffusivity, D scaled with polymer length, N as $D \propto N^{-2.3}$. Even with modern day parallel computers, brute-force equilibration of well-entangled branched polymers is prohibitively expensive. Standard method in which one starts with an ensemble of chains with the correct end-to-end distance arranged randomly in the simulation cell and introduces the excluded volume rapidly, leads to deformation on the intermediate length scales. Another set of long-standing methods includes the chain connectivity altering algorithms. These bridging methods employ a set of complex Monte Carlo (MC) moves that can be difficult to implement for branched polymer architectures and these MC moves have very low acceptance ratio (1, 2).

New preparation protocol has been established to overcome the described difficulties. This protocol is general to any polymer architecture and does not bring any deformation of polymer chains. Short simulation runs with soft potential used in Dissipative Particle Dynamics (DPD) (3) is performed for an ensemble of polymer chains with the correct end-to-end distance. After a gradual increase of the strength of DPD potential, short simulation with target coarse-grained potential is performed.

In this report, we adopt our method for two coarse-grained models 1) Kremer-Grest model (4) and 2) DPD model with Segmental Repulsive Potential (mSRP) (5). However, the described protocol is general and applicable for any coarse-grained model.

The present preparation method exploits two programs: *gel* and Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). *Gel* is an in house written C program of coarse-grained polymer builder, and LAMMPS is a molecular dynamics program from Sandia National Laboratories (6).

2. Models

2.1 Kremer-Grest Model

Kremer-Grest model: The pair interaction between topologically nonconnected particles is described by the standard truncated Lennard-Jones pair potential:

$$U_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 - \left(\frac{\sigma}{r_c} \right)^{12} + \left(\frac{\sigma}{r_c} \right)^6 \right], \text{ where } \epsilon \text{ is the depth of the potential well and } \sigma \text{ is}$$

the distance where interparticle force is zero. r_c represents the cutoff distance. $r_c = 2^{1/6} \sigma$ is

chosen, yielding so-called Weeks-Chandler-Andersen excluded volume potential, U_{WCA} . Topologically bound monomers interact according to the standard FENE/Lennard-Jones bonded potential, $U_{FENE/LJ}$. $U_{FENE/LJ}(r) = U_{FENE}(r) + U_{WCA}(r)$ and $U_{FENE}(r) = -\frac{a}{2} R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right]$, where standard parameter values for of $R_0 = 1.5 \sigma$ and $a = 30 \epsilon/\sigma^2$.

To model different flexibility of polymer chains, a bending potential of form $U_{bend}(r) = k_\theta (1 - \cos \theta)$ is employed, where θ is the angle between two neighboring bonds and k_θ is the bending constant. The detailed model description can be found in the original paper (4).

DPD model used as the first step. The pair interaction between topologically nonconnected particles is described by soft potential $U_{DPD}(r) = \frac{a_{DPD}}{2} \left(1 - \frac{r}{r_c} \right)^2$, where $a_{dpd} = 25 k_B T$ and $r_c = 1$ in DPD units of length are standard DPD parameters (3). Topologically bound monomers interact according to the standard FENE/Lennard-Jones bonded potential, $U_{FENE/LJ}$.

$U_{FENE/LJ}(r) = U_{FENE}(r) + U_{WCA}(r)$ and $U_{FENE}(r) = -\frac{a}{2} R_0^2 \ln \left[1 - \left(\frac{r}{R_0} \right)^2 \right]$, where standard parameter values for of $R_0 = 1.5 \sigma$ and $a = 30 \epsilon/\sigma^2$.

2.2 DPD Polymer Model with mSRP

The pair interaction between topologically nonconnected particles is described by soft potential

$U_{DPD}(r) = \frac{a_{DPD}}{2} \left(1 - \frac{r}{r_c} \right)^2$ where a_{dpd} is the maximum repulsion in $k_B T$ units and $r_c = 1$ in DPD

units of length. Topologically bound monomers interact according to the harmonic potential,

U_{harm} . $U_{harm}(r) = \frac{k}{2} (r - r_0)^2$, where k is the harmonic constant and r_0 is the equilibrium bond

distance. In order to avoid bond shrinkage and make a distance between bonded particles close to the distance between nonbonded particles, the values of $k = 225 k_B T/\rho$ and $r_0 = 0.85 r_c$ are used.

Chains crossing as a result of soft DPD potential is greatly reduced by introducing the Segmental

Repulsive Potential (mSRP), $U_{SRP}(r) = \frac{a_{SRP}}{2} \left(1 - \frac{d}{d_c} \right)^2$. The potential is effective for any pair of

bonds of the distance between midpoints of interacting bonds, d within cutoff, d_c with exception of neighboring bonds (no repulsion). The repulsion is equally divided between beads composing the bond. The values of $a_{SRP} = 100 k_B T$ and $d_c = 0.8 r_c$ significantly decrease the number of topological violations. As a result of absence of bond repulsion between two neighboring bonds and soft nonbonded potential, the value of average bond angle θ becomes greater than $\pi/2$.

Addition of bending potential $U_{bend}(r) = k_\theta (1 - \cos \theta)$ resolves this problem. The value $k_\theta = 2$

$k_B T$ is enough to compensate the action of mSRP potential and polymer behaves as a flexible chain. In depth explanation can found is in the original paper (5)

During all steps of our melt preparation we have used DPD thermostat on pairwise interactions. In a DPD simulation of polymers, particles interact with each other via a pairwise, two-body, short-ranged force, \mathbf{F} , that is written as the sum of a conservative force, \mathbf{F}^C , dissipative force, \mathbf{F}^D , and random force, \mathbf{F}^R , as follows: $\mathbf{F}_i = \sum_{j \neq i} \mathbf{F}_{ij}^C + \sum_{j \neq i} \mathbf{F}_{ij}^D + \sum_{j \neq i} \mathbf{F}_{ij}^R$. For a more detailed description of the DPD thermostat, see the original papers by Hoogerbrugge and Koelman (7) and Español and Warren (8).

3. Generation of Initial Structure Using *gel*

3.1 Theoretical

To equilibrate a polymer structure, it is necessary to generate an ensemble of polymer chains with the correct end-to-end distance (l).

Polymer chains are generated inside a periodic cubical box with the correct end-to-end distance $R^2(N) = l^2 C_N (N-1)$ on large length scales (N is large), where N is a number of beads, l is a bond distance and C_N is Flory characteristic ratio and $C_N = C_\infty$ at $N \rightarrow \infty$. For a Gaussian chain with a small bond angle θ the average cosine is $\langle \cos \theta \rangle = \frac{C_\infty - 1}{C_\infty + 1}$. For example, fully flexible

Lennard-Jones chains with $r_c = 2^{1/6} \sigma$ have $C_\infty = 1.88$ and DPD/SRP polymers have $C_\infty = 1.32$. Chains are built via a random walk in 3D space with either a desired angle or a random angle $\alpha = \pi - \theta$, that is sampled around $\langle \cos \alpha \rangle$. Bead number density of Kremer-Grest system, $\rho = 0.85 \sigma^{-3}$ and of DPD/SRP system $\rho = 3 r_c^{-3}$, which is a standard density for coarse-grained polymeric melts for these models, respectively.

3.2 Software Description

Program *gel* generates melts, blends and solutions. Polymer chains may include several blocks of different types of beads and/or angles. Different types of beads are used to drive a phase separation. Possible architectures include unconnected beads, linear chains, star-branched polymers with equal and unequal arm lengths, combs, dendrimers and hybrid star/comb/dendrimer structures. Chains are modeled as flexible, semi-flexible or rigid. Figure 1 shows the schematic picture of polymer architectures.

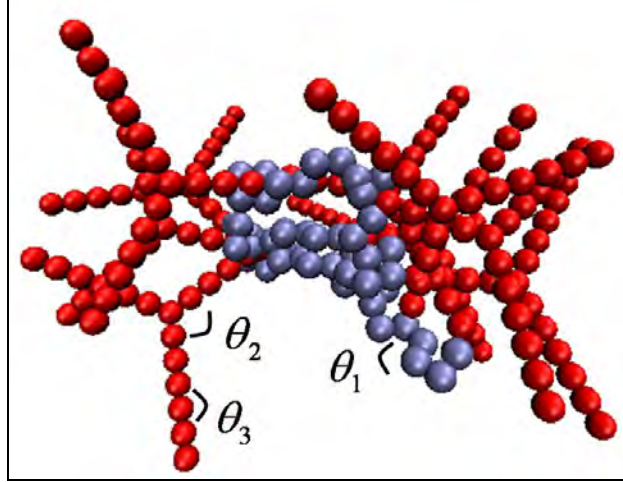


Figure 1. Schematic representation of bead-spring branched block copolymer. Different colors correspond to the different types of beads. The picture corresponds to example 1.

Source code: *gel.c*.

Arguments: $L_x, L_y, L_z, R, N_{rep}$. Where L_x, L_y, L_z are the dimensions of a periodic simulation box, R is equilibrium length of the bond and is N_{rep} a number of replicas. Value of R is taken with respect to the bond potential, for example FENE bond has $R \approx 0.9655\sigma$.

Input: *input* is a topology file (written by a user)

Input file	Commentaries
#molecules <input type="checkbox"/>	Number of molecular species
# atomtypes <input type="checkbox"/>	Number of bead types
#angletypes <input type="checkbox"/>	Number of angle types
#polymer1 <input type="checkbox"/>	Number of molecules of polymer 1
polymer1 <input type="checkbox"/> <input type="checkbox"/>	Number of arms (sidechains) in a polymeric units at the same branch point and number of repeated units
chain1 <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	Number of blocks, repeated units and an indicator of subbranches in the first arm (sidechain). The first arm always represents a main chain (backbone). The indicator equal 0 means that there are no subbranches. The indicator =1 means that there are subbranches at the end of this chain (branch point).
<input type="checkbox"/>	
<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	Type and number of beads and cosine, case and type of angle, α in the first block. Case = 0 is a random angle (with average cosine), case = 1 is a regular angle and case =2 is a special case for barbed wire (all 3 angles are 120°)
.....	
branch1 <input type="checkbox"/> <input type="checkbox"/>	Number of arms (sidechains) in a substar and number of repeated units
subchain1 <input type="checkbox"/> <input type="checkbox"/>	Number of blocks, repeated units and an indicator of subbranches in the first substar. The first arm always represents a main chain. The indicator is always 0.
<input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	Type and number of beads and cosine, case and type of angles in the first block. Case = 0 is a random angle (with average cosine), case = 1 is a regular angle and case =2 is a special case for barbed wire (all 3 angles are 120 °)

Output: *data_i.chain* and *snap_i.xyz* files, where $i = 0, \dots, N_{rep} - 1$. *data_i.chain* is topology file for LAMMPS software. *snap_i.xyz* is xyz file for Visual Molecular Dynamics (VMD) software (for a visual checking). VMD is a molecular visualization program for displaying, animating, and analyzing large biomolecular systems using 3-D graphics and built-in scripting.

To run the code, a user has to have *gel.c* and *input* files in a working directory. *gcc* compiler could be used for compiling, as *gcc gel.c -o gel -lm*. The user has to write *input* to define a desirable topology.

In the following example the code generates 3 replicas of a blend of linear flexible chains, composed of 500 chains of 250 beads and 250 chains of 500 beads. The periodic box size is 66.5×66.5×66.5 and bond length is 0.9655.

```
#molecules 2
#atomtypes 1
#angletypes 0
#polymer1 500
polymer1 1 1
```

```

chain1 1 1 0
1 250 -0.303135889 0 0
#polymer2 250
polymer2 1 1
chain1 1 1 0
1 500 -0.303135889 0 0

```

To run the user has to type `./gel 66.5 66.5 66.5 0.9655 3`. This action will produce the following output files: *data_0.chain*, *data_1.chain*, *data_2.chain* and *snap_0.xyz*, *snap_1.xyz*, *snap_2.xyz*.

The following are examples of input files for several possible branched structures:

Example 1. “Barbed wire” polymer (see figure 1).

```

#molecules 1
#atomtypes 2
#angletypes 2
#polymer1 1
polymer1 2 2
chain1 1 1 0
2 2 -0.303135889 0 0
chain2 2 1 1
1 1 -0.303135889 0 0
1 1 -1.0 1 1
branch1 2 1
subchain1 2 1 0
1 1 -0.5 2 2
1 1 -1.0 1 1
subchain2 2 1 0
1 1 -0.5 2 2
1 1 -1.0 1 1

```

Example 2. Dendrimer. Some of angles are set to 180° to make visualization easier (see figure 2).

```

#molecules 1
#atomtypes 5
#angletypes 2
#polymer1 1
polymer1 6 1
chain1 1 1 1
1 10 -1.0 1 1
chain2 1 1 1
1 10 -1.0 1 1
chain3 1 1 1
2 5 -1.0 1 1
chain4 1 1 1
2 5 -1.0 1 1

```

chain4 1 1 1
4 10 -1.0 1 1
chain5 1 1 1
4 10 -1.0 1 1
branch1 3 1
subchain1 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain2 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain3 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
branch2 3 1
subchain1 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain2 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain3 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
branch3 5 1
subchain1 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain2 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain3 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1
3 4 -0.303135889 0 0
subchain4 3 1 0
3 1 -0.5 1 2
3 1 -1.0 1 1

3 4 -0.303135889 0 0
 subchain5 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 branch4 5 1
 subchain1 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain2 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain3 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain4 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain5 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 branch5 2 1
 subchain1 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0
 subchain2 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0
 branch6 2 1
 subchain1 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0
 subchain2 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0

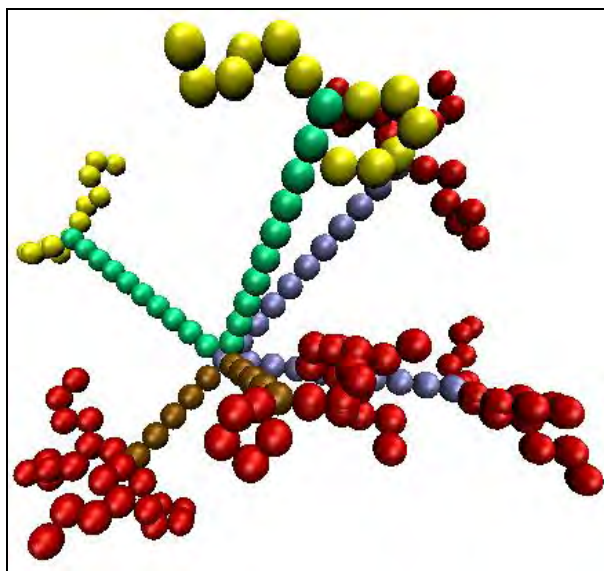


Figure 2. Bead-spring dendrimer. Different colors correspond to the different types of beads. The picture corresponds to example 2.

Example 3. Comb/dendrimer. Some of angles are set to 180 and 120° to make visualization easier (see figure 3).

```
#molecules 1
#atomtypes 6
#angletypes 2
#polymer1 1
polymer1 7 10
chain1 1 1 0
6 40 -0.303135889 0 0
chain2 1 1 1
1 10 -1.0 1 1
chain3 1 1 1
1 10 -1.0 1 1
chain4 1 1 1
2 5 -1.0 1 1
chain5 1 1 1
2 5 -1.0 1 1
chain6 1 1 1
4 10 -1.0 1 1
chain7 1 1 1
4 10 -1.0 1 1
branch2 3 1
subchain1 3 1 0
3 1 -0.5 1 2
```

3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain2 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain3 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 branch3 3 1
 subchain1 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain2 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain3 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 branch4 5 1
 subchain1 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain2 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain3 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain4 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain5 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 branch5 5 1
 subchain1 3 1 0

3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain2 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain3 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain4 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 subchain5 3 1 0
 3 1 -0.5 1 2
 3 1 -1.0 1 1
 3 4 -0.303135889 0 0
 branch6 2 1
 subchain1 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0
 subchain2 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0
 branch7 2 1
 subchain1 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0
 subchain2 3 1 0
 5 1 -0.5 1 2
 5 1 -1.0 1 1
 5 4 -0.303135889 0 0

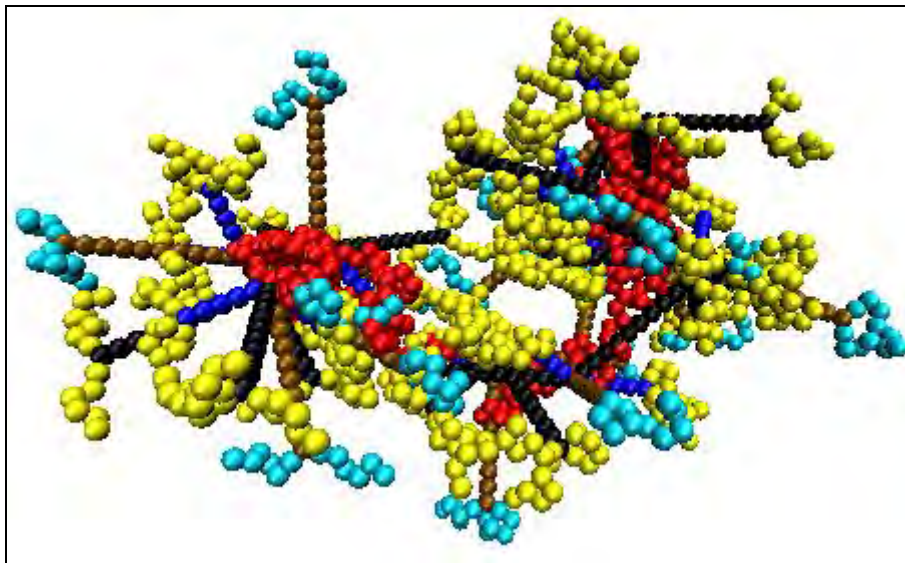


Figure 3. Bead-spring dendrimer/comb polymer. Different colors correspond to the different types of beads. The picture corresponds to example 3. Some side chains are built to be rigid.

4. Equilibration of the Initial Structures

Short simulation runs with soft potential used in DPD have been performed for an ensemble of polymer chains with the correct end-to-end distance. DPD potential allows chains to pass through each other to speed up the polymer dynamics. Simulation with DPD potential deforms the chains on the intermediate length scales. However, this deformation is fully resolved after $500 \tau_{DPD}$. After this step, the following procedures are adopted for two coarse-grained models 1) Kremer-Grest model (4) and 2) DPD model with Segmental Repulsive Potential (mSRP) (5)

Kremer-Grest model. Next step is a gradual increase of the strength of DPD potential in order to increase distance between nonbonded monomers or “push-off”. Finally, DPD potential is substituted to full Lennard-Jones potential. This step does not significantly alter the structural properties of the melt. Finally, the melt is simulated with Lennard-Jones potentials for time equal to $10000 \tau_{LJ}$ to remove DPD alterations of structural properties on the short length scale.

DPD with mSRP model. mSRP and bending potential (see section 2) are added and the melt are equilibrated for time = $1000 \tau_{DPD/mSRP}$ to remove DPD alterations of structural properties on the short length scale.

To equilibrate the initial structure one has to use LAMMPS software. To run LAMMPS, a user has to copy *data.chain* produce by *gel* program in a working directory. The following are input scripts for LAMMPS for Kremer-Grest and DPD with mSRP models, respectively.

Kremer-Grest model.

```
units      lj
atom_style bond
special_bonds lj/coul 0 1 1
read_data  data.chain
neighbor    0.4 bin
neigh_modify every 1 delay 1
communicate single vel yes
bond_style fene
bond_coeff  1 30.0 1.5 1.0 1.0
dump mydump all custom 100000 chain_un*.xyz id type xu yu zu
fix         1 all nve
timestep    0.01
thermo 1000
pair_style  dpd 1.0 1.0 122347
pair_coeff   * * 25 4.5 1.0
velocity all create 1.0 17786140
run         50000
write_restart my_restart_dpd
pair_coeff   * * 50.0 4.5 1.0
velocity all create 1.0 15086120
run         50
pair_coeff   * * 100.0 4.5 1.0
velocity all create 1.0 15786120
run         50
pair_coeff   * * 150.0 4.5 1.0
velocity all create 1.0 15486120
run         50
pair_coeff   * * 200.0 4.5 1.0
velocity all create 1.0 17986120
run         100
pair_coeff   * * 250.0 4.5 1.0
velocity all create 1.0 15006120
run         100
pair_coeff   * * 500.0 4.5 1.0
velocity all create 1.0 15087720
run         100
pair_coeff   * * 1000.0 4.5 1.0
velocity all create 1.0 15086189
run         100
write_restart my_restart_dpd1
pair_style hybrid/overlay lj/cut 1.122462 dpd/tstat 1.0 1.0 1.122462 122347
pair_modify shift yes
pair_coeff * * lj/cut 1.0 1.0 1.122462
pair_coeff * * dpd/tstat 4.5 1.122462
velocity all create 1.0 15086120
```

```

run          50
velocity all create 1.0 15086121
run          50
velocity all create 1.0 15086111
run          50
write_restart my_restart_push
velocity all create 1.0 15086125
run          1000000
write_restart my_restart_lj

```

DPD with mSRP model.

```

units        lj
atom_style    angle
special_bonds lj/coul 1 1 1
newton on off
read_data     data.chain
neighbor       2.5 bin
neigh_modify  every 1 delay 1
communicate single vel yes
# syntax for bond-bond pair_style
# use hybrid/overlay with regular dpd
# dpdbb <cutoff> <distance: min=0 midpoint=2> <search for top volations: no=0 ye
s=1> <skin distance>

```

```

bond_style     harmonic
bond_coeff     1 225.0 0.85
pair_style     dpd 1.0 1.0 373692
pair_coeff      * * 60.0 4.5 1.0
velocity all create 1.0 17786140
dump mydump all custom 10000 chain_dpd*.xyz id type x y z
thermo 1000
fix            1 all nve
timestep       0.01
run            50000
write_restart my_restart_dpd
velocity all create 1.0 40783012
undump mydump
pair_style     hybrid/overlay dpd 1.0 1.0 373692 dpdbb 0.8 2 0 2.5

```

```

# syntax for bond-bond pair_coeff
# bondtype bondtype a0 cutoff(optional)

```

```

pair_coeff      * * dpdbb * * 100.0 0.8
pair_coeff      * * dpd 60.0 4.5 1.0
angle_style     cosine
angle_coeff     1 2.0

```

```
dump mydump1 all custom 10000 chain*.xyz id type x y z  
restart 10000 periodic_restart  
run 100000  
write_restart my_restart_1
```

5. Results

In order to characterize the chain conformations in the melt after push-off, the authors performed calculations of mean square internal distances of chains $\langle R^2(n) \rangle / n$ is averaged over all possible combinations of segments of size $n = |i - j|$ along the chains, where $i < j \in [1, N]$ are monomer indices. This metric is an excellent indicator of chain configuration at all length scales. Code `msid_1.c` is used to calculate this function. Arguments are $N, a, N_{tot}, file1, file2$, where N is a number of monomers per chain, a is a size of the cubical periodic box, N_{tot} is a total number of particles, *file1* is an input name and *file2* is an output name. For example, `./msid_1 500 66.5 250000 snap_lj.xyz lj_msid`. Note: input files should be in VMD xyz format. To show that our preparation technique produced a sample with topology equivalent to the well-equilibrated structure, we applied our method to a melt of $M = 500$ chains of $N = 500$ beads. Simulation box was $66.5 \times 66.5 \times 66.5 \sigma^3$. We compared a topology of 1) the melt produced by our method or 2) the melt equilibrated by running MD simulation for time long enough that the chains moves 3 times their own size (the run time was $t = 6.5 \times 10^6 \tau_{LJ}$). Figure 4 shows the results

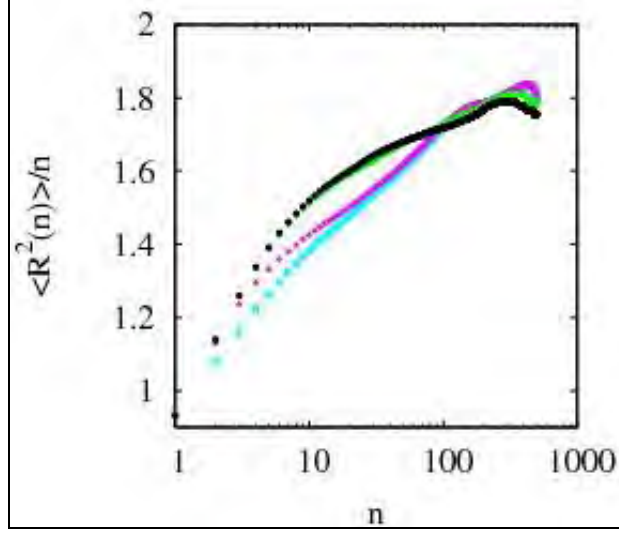


Figure 4. Evolution of mean square internal distances for a melt of chain length $N = 500$ throughout our preparation procedure. Blue, red and green symbols correspond to the chains after initial $1000 \tau_{\text{DPD}}$ simulation with the soft (DPD) potential, after fast “push-off” and after $10000 \tau_{\text{LJ}}$ simulation with Lennard-Jones potential, respectively. The black symbols denote our target function obtained for the equilibrated melt, where simulation time is $t = 6 \times 10^6 \tau_{\text{LJ}}$.

Using geometrical analysis, the authors estimated the entanglement length, N_e by running Z1code (9). The authors found that N_e for an equilibrated and prepared system is 83 and 84, respectively.

The results demonstrate the excellent agreement between structural properties of the melts generated via our method and brute-force equilibration.

6. References

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